(+) Entropy S

Obtained as above from

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$F = -NkT \ln Z$$

Gives $$S = Nk \left\{ \ln\left(\frac{\exp(h\nu/kT)}{[\exp(h\nu/kT)-1]}\right) + \frac{(h\nu/kT)}{[\exp(h\nu/kT)-1]} \right\}$$

Comparison to real systems.

1. Vibration of N atoms in solid.

Can change from 1D → 3D vibrations by considering 3N oscillators

Snag In solid atomic vib^{ns} not independent.

Independent — just one freq ν

Coupled — range of freq$_s$

Nevertheless.

Have developed quantum mechanical model for vib^n of atoms in solid.

Our approx — just one value ν

→ Einstein model.

(Range of ν values — simplest treatment - Debye).

Einstein model.

Successes

(i) High temp value $C_v \rightarrow 3Nk$

(ii) As $T \rightarrow 0$ $\quad C_v \rightarrow 0$

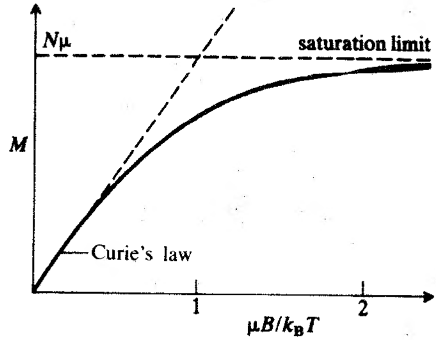
Failures

Does not predict correct shape for C_v versus T between above limits

Comparison — see sheet.

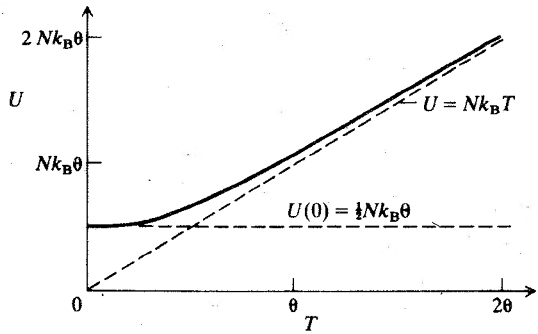
Paramagnetic solid

M versus $\left(\frac{\mu B}{kT}\right)$

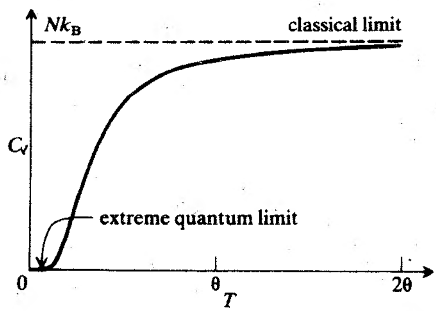


System of N one dimensional oscillators.

Energy.



Heat Capacity



Quantum and classical limits

At temp T mean energy ration for each energy mechanism is kT.

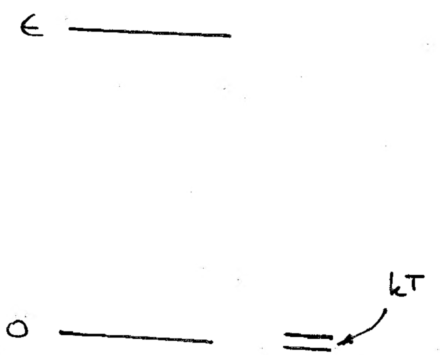
But energy mechanisms have their own (quantised) energy scale.

Eg harmonic oscillator $\epsilon = j h\nu$

ν depends on mechanical properties of oscillator.

Relation between ϵ and kT determines quantum or classical behaviour.

(i) If $\epsilon \gg kT$

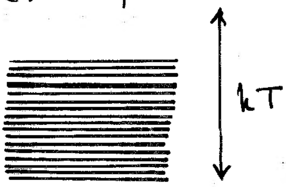


Quantum behaviour

most systems $\epsilon = 0$

few $\epsilon = \epsilon$

(ii) If $\epsilon \ll kT$



Classical limit

ϵ levels so closely packed they approach continuum.

In above analyses get changes in U, C_v, S when $kT \sim \epsilon$

In reverse if measure C_v versus T – get features in graph at temp T where $kT \sim$ energy level spacing.

Non-localised particles.

Gases.

From quantum mechanics of particles in a box of side L — get expression for density of states

$g(\epsilon)\,d\epsilon$ = number of energy states between $\epsilon \to \epsilon + d\epsilon$.

Particle in box - side L

Quantum mechanics

- particle represented by wavef^n ψ
- must obey boundary conditions

Standing wave boundary conditions

Require $\psi = 0$ at $x, y, z = 0$
$= L$

Recall

$$\psi = A \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

normalisn.

At $x, y, z = 0$

$\sin(\ )$ ensures $\psi = 0$

At $x = L$

$\psi = 0$ for $k_x . L = \pi n_x$

$$k_x = \frac{\pi n_x}{L}$$

$$k_y = \frac{\pi n_y}{L}$$

$$k_z = \frac{\pi n_z}{L}$$

where n_x, n_y, n_z are positive integers

W/f $\psi = A \sin\left(\frac{\pi}{L} n_x . x\right) \sin\left(\frac{\pi}{L} n_y . y\right) \sin\left(\frac{\pi}{L} n_z . z\right)$

is standing wave in box specified by quantum numbers n_x, n_y, n_z.

Representation in k space

Diagram — see sheet.

Points.

(i) Points at $\frac{\pi}{L} n_x$, $\frac{\pi}{L} n_y$, $\frac{\pi}{L} n_z$ denote allowed states.

(ii) Characteristic spacing $= \pi/L$

Note – if particle confined within atomic dimension a —

spacing of states $\sim \pi/$

For gases since enclosure $L \sim 10^9 a$

Spacing of states very small.

Small spacing $\longrightarrow$ classical case

π/a spacing $\longrightarrow$ quantum " .

Density of states in k space.

Number of states with k components in range

$k_x \rightarrow k_x + dk_x$

$k_y \rightarrow k_y + dk_y$

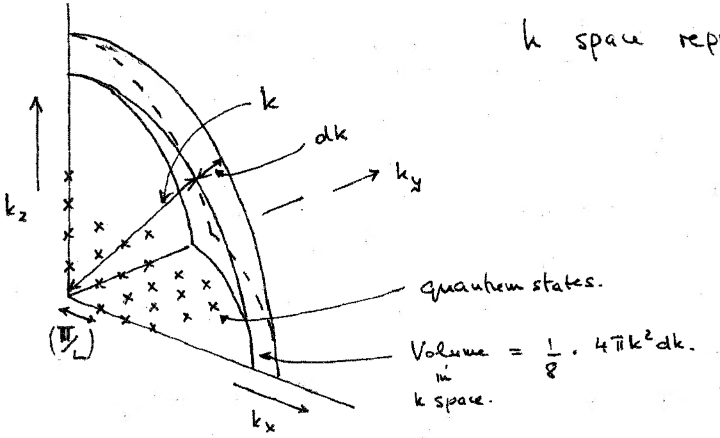
$k_z \rightarrow k_z + dk_z$ written as

$$g(k_x, k_y, k_z)\, dk_x\, dk_y\, dk_z = \frac{dk_x\, dk_y\, dk_z}{(\pi/L)^3}$$

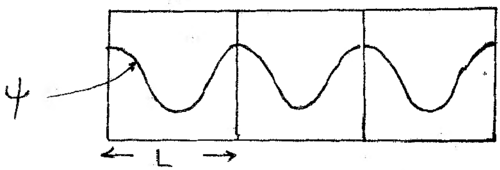
Volume of k space.

Standing wave boundary conditions.

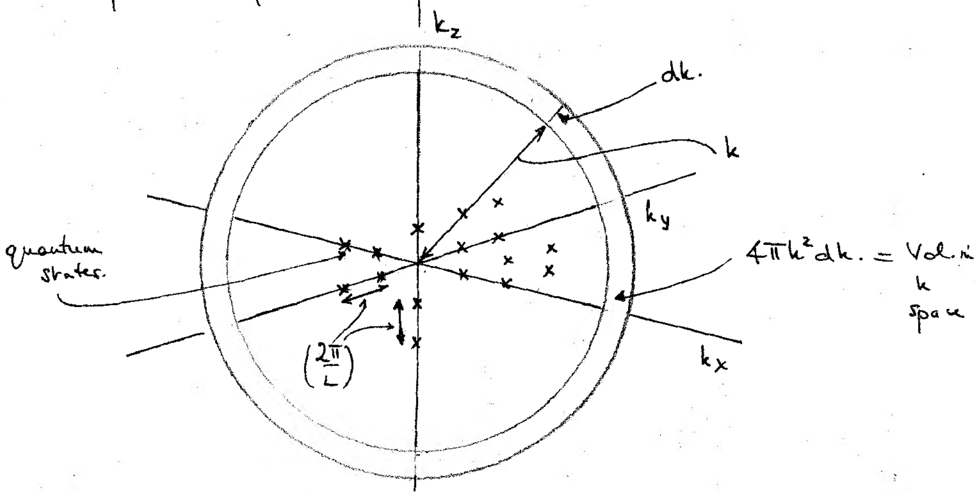
k space representation.



Periodic Boundary conditions.



k space representation



Number of states with $k \longrightarrow k + dk$ (all directions).

$$g(k)\,dk = \frac{1}{8} \cdot \frac{4\pi k^2\,dk}{(\pi/L)^3}$$

where $\frac{1}{8} \cdot 4\pi k^2\,dk$ = vol in k space. See sheet.

$$g(k)\,dk = \frac{L^3 \cdot 4\pi k^2\,dk}{(2\pi)^3}$$

$$g(k)\,dk = \frac{V \cdot 4\pi k^2\,dk}{(2\pi)^3}$$

Proved for case of $V = L^3$ (cube) but is generally true for V of any shape.

Travelling wave boundary conditions.

Moving particles — use wave f^n ψ

$$\psi = A \exp(ik_x x) \exp(ik_y . y) \exp(ik_z . z)$$

Boundary condition — periodic - see sheet.

Condition - w/f repeats in length of box.

For x dir^n.

$$A \exp(ik_x . x) = A \exp(ik_x . (x+L))$$

$$\cancel{\exp(ik_x . x)} = \cancel{\exp(ik_x . x)} . \exp(ik_x . L)$$

$$1 = \exp(ik_x . L)$$

Requires $k_x . L = 2\pi n_x$ $\qquad k_x = \frac{2\pi n_x}{L}$

likewise $k_y . L = 2\pi n_y$ $\qquad \therefore k_y = \frac{2\pi n_y}{L}$

Now $n_x, n_y, n_z = \pm 1, \pm 2 \ldots$

Representation in k space — see sheet.

(51)

Here

(i) n_x, n_y, n_z now take $\pm$ integer values

(ii) Spacing $(2\pi/L)$.

Density of states

$$g(k)\,dk = \frac{4\pi k^2\,dk}{(2\pi/L)^3}$$

$$= \frac{V.\ 4\pi k^2\,dk}{(2\pi)^3} \quad \text{– as before}$$

Density of states in energy $g(\epsilon)\,d\epsilon$

Want connection

$$g(k)\,dk \longrightarrow g(\epsilon)\,d\epsilon$$

Need relation between ϵ and k – dispersion relation

This depends on system.

Particle mass m – all energy kinetic translation

Then $\epsilon = \dfrac{p^2}{2m}$ $\quad p$ = momentum

Previous quantum mechanics $p = \hbar k$

$$\epsilon = \frac{\hbar^2 k^2}{2m}$$

$$k = \left(\frac{2m\epsilon}{\hbar^2}\right)^{1/2}$$

53

$$dk = \frac{1}{2}\left(\frac{2m}{\hbar^2}\right)^{1/2} \epsilon^{-1/2}\, d\epsilon$$

Then

$$g(k)\,dk = \frac{V}{(2\pi)^3} \cdot 4\pi k^2\, dk$$

$$g(\epsilon)\,d\epsilon = \frac{V}{(2\pi)^3} \cdot 4\pi \left(\frac{2m\epsilon}{\hbar^2}\right) \cdot \frac{1}{2}\left(\frac{2m}{\hbar^2}\right)^{1/2} \frac{d\epsilon}{\epsilon^{1/2}}$$

$$g(\epsilon)\,d\epsilon = \frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2}\, d\epsilon$$

Points

(i) This for 3D system – easy to get 2D and 1D expressions

(ii) $\epsilon = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$

54

$$\epsilon = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right)$$

Energy spacing $\Delta\epsilon = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 \Delta n^2$

For He gas in box $L = 0.3\,m$

$\Delta n^2 = 1$

$m = 4 \times 1.66 \times 10^{-27}$ kg

$\Delta\epsilon = 3.8 \times 10^{-40}\,J \equiv 2.4 \times 10^{-21}\,eV$

At 300 K then $kT \equiv 0.025\,eV$

Thus $kT \gg \Delta\epsilon$ classical limit.

(iii) Spin.

Particle with spin needs extra quantum number

If G different spin states - include in density of states

$$g(\epsilon)\,d\epsilon = \frac{G \cdot V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2}\,d\epsilon$$

Thermal distributions for different kinds of gas.

Gases — Large number of weakly interacting, indistinguishable particles confined in a macroscopic enclosure.

Different kinds

(i) Fermi - Dirac gas

(ii) Bose - Einstein gas

(iii) Boltzmann gas.

Distribution

Variation of number of particles n_j in state of energy ϵ_j

or

probability of population $f(\epsilon_j)$ for state of ϵ_j

Method

Step 1. Single particle states – in gas very close together

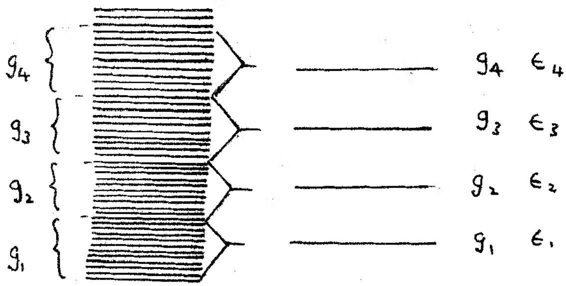
Step 2. Possible distributions

Convenient to clump energy states ϵ_j into wider spaced levels ϵ_i each with degeneracy g_i

Diagram – see sheet.

States to levels.

States (j) Levels (i)



Distribution now $\{n_i\}$ n_i particles in level ϵ_i

Works if

(i) g_i very large

(ii) level spacing $\Delta\epsilon_i \ll kT$.

For case of He atoms (Guenault)

For $g_i = 10^{10}$

Have $\Delta\epsilon_i \sim 10^{-9}. kT$.

Conditions satisfied

Step 3 Count microstates for each possible distribution.

First – recap on Fermi-Dirac and Bose-Einstein particles.

Microstate of 2 indistinguishable particles – $\psi(1,2)$

When particles exchanged $1 \rightleftarrows 2$

How is $\psi(2,1)$ related to $\psi(1,2)$?

Indistinguishable $|\psi(2,1)|^2 = |\psi(1,2)|^2$

allows 2 solutions

$$\psi_S(2,1) = +\psi(1,2) \quad - \text{symmetric}$$

$$\psi_A(2,1) = -\psi(1,2) \quad - \text{antisymmetric}$$

Writing as weakly interacting particles 1, 2 in states a, b

$\psi(1,2)$ cannot be $\psi_a(1)\psi_b(2)$ - not indistinguishab[le]

Have to write

$$\psi_s(1,2) = \frac{1}{\sqrt{2}}\left\{\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)\right\}$$

$$\psi_A(1,2) = \frac{1}{\sqrt{2}}\left\{\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)\right\}$$

ψ_s - symmetric - Bose Einstein particles

ψ_A - antisymmetric - Fermi Dirac particles.

Crucial difference put $a = b$

Bosons $\psi_s = \sqrt{2}\,\psi_a(1)\psi_a(2)$

Fermions $\psi_A = 0$

Pauli exclusion principle - no two fermions can occupy same quantum state

Examples

Fermions — spin $1/2$, $3/2$ ...

- electrons, protons, neutrons, He^3 atoms

Bosons — spin 0, 1 ...

- photons, Cooper pairs, He^4 atoms..

Return to deriving distribution for separate cases.

Fermions.

Count microstates of n_i particles in level of ϵ_i and degeneracy g_i

n_i ——— g_i ϵ_i Level has g_i states.

Each state occupied or unoccupied

n_i states occupied

$(g_i - n_i)$ states unoccupied